



Hydrothermal liquefaction for algal biorefinery: A critical review



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ARTICLE INFO

Article history:

Received 7 November 2013

Received in revised form

9 May 2014

Accepted 6 July 2014

Available online 26 July 2014

Keywords:

Hydrothermal liquefaction

Algal biorefinery

Biocrude oil

Algal biofuel

ABSTRACT

Hydrothermal liquefaction (HTL) has recently received increasing attention due to its advantages in rapid reaction, using wet feedstocks with no lipid-content restriction. These characteristics make HTL especially suitable for conversion of algae into biocrude oil. This paper aims to provide a state-of-the-art review of HTL technologies from a perspective of algal biorefinery. In this review, we first summarize the updated researches and technologies of algae HTL. Specially, an “Environment-Enhancing Energy” (E2E) paradigm based on algal biorefinery has been proposed and discussed. Second, the principles and crucial factors for algae HTL are discussed with focus on (1) algae species and characteristics including lipids, proteins and carbohydrates; (2) the operational parameters including total solids, holding temperature, retention time and catalysts; and (3) the critical principles of HTL reaction and the role of deoxygenation and denitrogenation. In addition, potential applications of HTL are discussed. Prospective and challenges of HTL for algal biorefinery are finally addressed including feedstock preparation, scale-up of algae HTL, and process integration.

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Abbreviations: daf, dry ash-free basis; db, dry basis; E2E, Environment-Enhancing Energy; HHV, higher heating value; HTC, hydrothermal carbonization; HTL, hydrothermal liquefaction; HTG, hydrothermal gasification; TS, total solids

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<http://dx.doi.org/10.1016/j.rser.2014.07.030>

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1. Introduction

Algal biofuel has been proposed as the next generation biofuel [1–3]. The nature of algal biofuel is to convert sunlight into chemical energy through algae growth, which can be used as feedstocks for further biological or thermochemical conversion processes [4,5]. Among these processes, two main routes to produce liquid biofuels from algae are biodiesel via the extraction or transesterification [6], bio-oil via pyrolysis and biocrude oil via hydrothermal liquefaction (HTL) [4,7].

The HTL of algae is defined as the direct liquefaction of algal biomass into biocrude oil in a closed oxygen-free reactor by pressurizing inert gases (e.g., N_2 or He) or reducing gases (e.g., H_2 or CO), at a certain temperature (200–380 °C) and pressure (5–28 MPa) [8–12]. The hot compressed water in the HTL (i.e. sub-/near-critical water) is used for both solvent and reaction medium [13]. A continuous HTL process [14] in detail is presented in Fig. 1. Biocrude oil is the most important product, mainly consisting of hydrocarbons and O/N-containing compounds. Biocrude oil has the potential as feedstocks for co-refining in an existing fossil refinery to produce energy and chemicals [15–17]. Besides

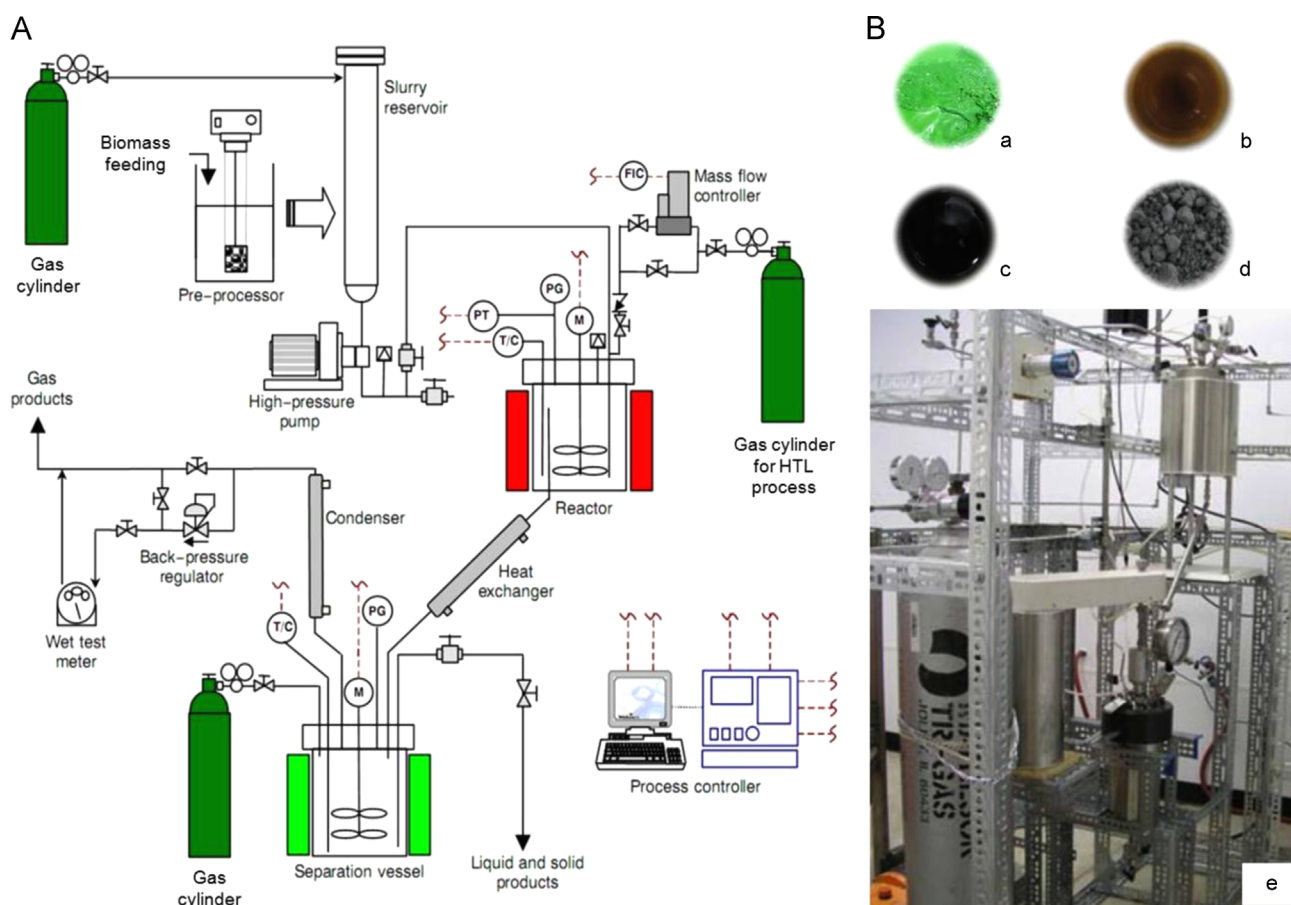


Fig. 1. A continuous hydrothermal liquefaction (HTL) process [14]. (A) A flowchart of HTL; and (B) pictures of algae HTL: (a) algae slurry, (b) aqueous products, (c) biocrude oil, (d) solid residue, and (e) HTL reactor.

biocrude oil, other products distributed in aqueous, gaseous, and solid phases are also released through HTL (Fig. 1). Compared to other conversion technologies such as oil extraction and pyrolysis [4,18], HTL of algae has some prominent characteristics [9–11]: (1) the process eliminates the drying process of feedstock, because the HTL demand for total solids (TS) of algal feedstock is usually 10–25%; (2) the whole algal biomass, not only lipids but also proteins and carbohydrates, can be converted to biocrude and chemicals, leading to a higher biocrude oil yield. For instance, Yu et al. [19] reported that an algae strain containing only 0.1% of lipids achieved a biocrude oil yield of as high as 39.0% via HTL; (3) high lipids content is also not a decisive factor of feedstock screening since HTL can convert the whole algae biomass; (4) mass transfer is enhanced using sub-/super-critical water as the reaction medium; (5) the enthalpy of phase change of water at high pressure (i.e. the hot compressed water is not in the form of vapor) is largely reduced, leading to a reduced latent loss and enhanced energy efficiency of HTL; and (6) principally products separation could be self-regulated by the control of operational conditions instead of additional rectification or extraction.

The concept of HTL for algal biorefinery was derived from the 1970s [20]. Elliott et al. [21] summarized the advances on direct thermochemical conversion of biomass to hydrocarbon fuels from 1983 to 1990. In the past two decades, hydrothermal conversion has attracted growing interests. Behrendt et al. [8] reviewed direct liquefaction (including solvolysis) especially for lignocellulosic biomass. Different conditions were then discussed, such as subcritical [9,11] or supercritical water [9], holding temperature and retention time at the holding temperature [10]. Recently, the importance of algae as a promising feedstock for HTL has been addressed [11,22]. Japan was one of the pioneering countries focused on this field, but ceased after 2005 [23–28]. More studies have been reported since 2010 due to the high price of petroleum [29,30]. A large number of publications had been concentrated in the US [19,31–44] since 2010. HTL of algae was also studied in other countries, such as the UK [45–47], China [48–54] and the Netherlands [41,55,56]. Besides academic activities, the US Department of Energy (2012) added HTL as one of

the five major pathways for biomass conversion technologies [57]. The US National Renewable Energy Laboratory (NREL) and Pacific Northwest National Laboratory (PNNL) (2013) have recently composed a technical report focused on “Whole Algae Hydrothermal Liquefaction Technology Pathway” [58].

Typical limitations for algal biofuel production are the consumption of water, nutrients, energy and environmental pollution [59]. One promising alternative is to reuse and recycle nutrients, wastewater and chemicals via the algal biorefinery [1,60–64]. Researchers have recently proposed a renewable algal biorefinery based on HTL of algae [37,41,65]. This concept was later formally proposed as “Environmental-Enhancing Energy” (E2E) [19,66–69] by Zhang [70]. E2E is established based on the full use of feedstock components by maximizing the recovery of hydrocarbon and reusing nutrients stored in post-HTL aqueous by algae cultivation. In E2E, biocrude oil is converted from algae via HTL; the post-HTL wastewater was cleaned and carbon dioxide is captured via algae cultivation; the augmented algal biomass will be further converted into biocrude oil via HTL. Thus, the E2E paradigm realizes multiple stages of algae production and biofuel conversion, and at the same time cleans wastewater and captures carbon dioxide.

Based on the analysis of literature, this review aims to summarize the updated research and technologies of HTL of algae, so that the systematic fundamentals of E2E are elucidated. The principles and crucial factors for HTL of algae are discussed with the focus on feedstock types, process parameters and HTL product distribution. Prospective and challenges on the development and application of HTL of algae are finally discussed.

2. HTL for algal biorefinery

HTL is a process to convert algal biomass into four phases: biocrude oil, aqueous products, solid residue and gaseous products. To understand the process and full use of these products, a synergistic algal biorefinery, E2E is described in Fig. 2. There are three operational units in algae based E2E, including algal biomass

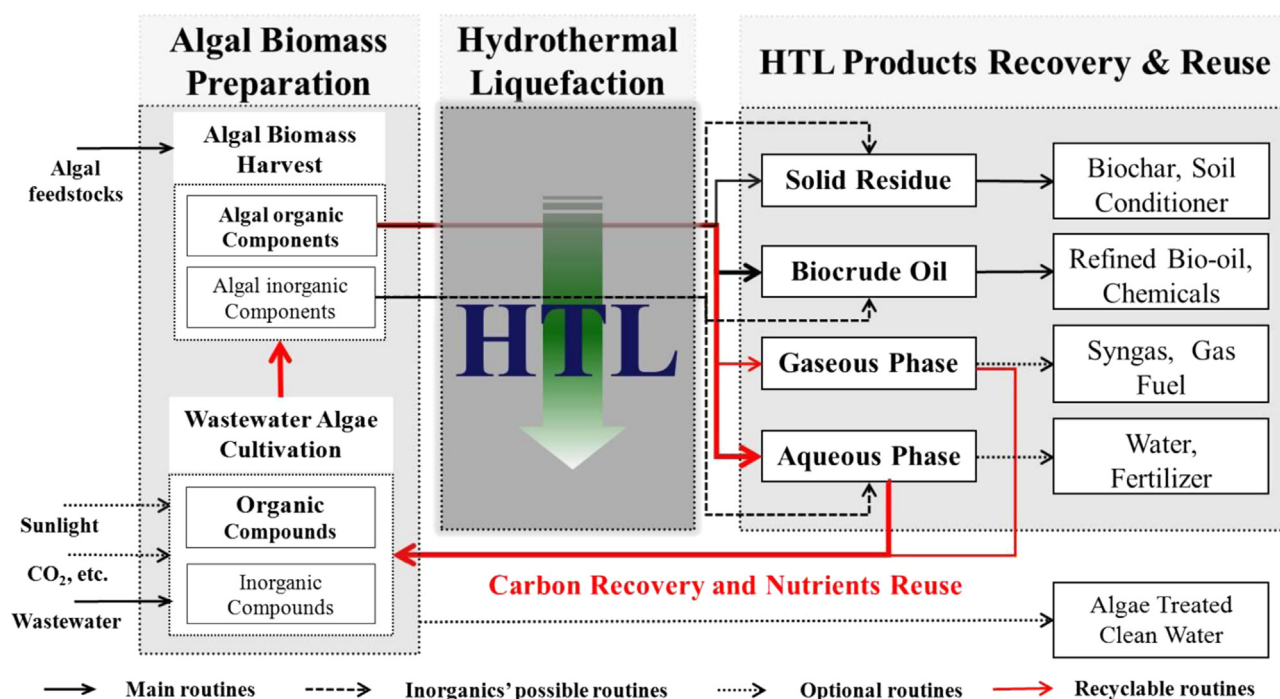


Fig. 2. A block diagram of Environment-Enhancing Energy (E2E) via HTL of algae. Figure was drawn derived from Refs. [19,37,58,66,70,81]. The E2E process includes three modules: algae biomass preparation (algae cultivation and harvest), HTL, and products recovery and reuse.

preparation, HTL reaction, and HTL products recovery and reuse. After HTL, nutrients (nitrogen, phosphorus, etc.) stored in post-HTL wastewater could be fed back for algae cultivation. CO₂ produced through HTL and/or released from other sources such

as the thermal power plant can be used for algae growth. The wastewater generated by the whole process besides HTL could also be collected for algae growth. In addition, the inorganic compounds also play an important role in the E2E scheme.

Table 1

Summary of the HTL operational conditions for algae biomass.

Algae species	Algae HHV*	Optimal conditions for biocrude oil yield	Oil yield (daf%)*	Optimal conditions for biocrude oil HHV*	Oil HHV*	Ref.
Pioneering time						
<i>Botryococcus branunii</i>	34.2 ^a	6%(TS)*; 300 °C, 60 min, Na ₂ CO ₃ , 2 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	64	6%(TS)*; 200 °C, 60 min, Na ₂ CO ₃ /300 °C, 60 min, 2 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	50.2 ^a	[23]
<i>Dunaliella tertiolecta</i>	19.8 ^a	22%(TS)*; 300 °C, 5 min, Na ₂ CO ₃ , 3 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	44	22%(TS)*; 340 °C, 5 min, 3 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	37.8 ^a	[24]
<i>Spirulina</i>	18.8 ^a	20% (TS)*; 350 °C, 60 min (H ₂ , 5 MPa); hexane extraction	78	20% (TS)*; 350 °C, 60 min (Toluene, H ₂ , 5 MPa); hexane extraction	33.2 ^a	[25]
Silent time						
<i>Microcystis viridis</i>	26.1 ^a	15% (TS)*; 340 °C, Na ₂ CO ₃ , 30 min, 3 MPa IP* (N ₂); CHCl ₃ extraction	33	15% (TS)*; 340 °C, 30 min; Na ₂ CO ₃ , 3 MPa IP* (N ₂); CHCl ₃ extraction	31 ^a	[28]
Renaissance time						
<i>Spirulina platensis</i>	19.6 ^a	10% (TS)*; 350 °C, 60 min; Na ₂ CO ₃ , 2 MPa IP* (N ₂); acetone extraction	48 ^c	10% (TS)*; 350 °C, 60min, 2 MPa IP* (N ₂); Acetone extraction	31.2 ^b	[31]
Mixed microalgae	16.3 ^a		23 ^c		36.6 ^b	
<i>Spirulina platensis</i>	16.3 ^a	20% (TS)*; 350 °C; 60 min, 2 MPa IP* (N ₂); acetone extraction	43 ^c	20% (TS)*; 380 °C, 60 min, 2 MPa IP* (N ₂); acetone extraction	39.9 ^b	[35]
<i>Spirulina platensis</i>	16.3 ^a	20% (TS)*; 350 °C; 60 min, Na ₂ CO ₃ , 2 MPa IP* (N ₂); acetone extraction	55 ^c	20% (TS)*; 350 °C, 60 min, Ca ₃ (PO ₄) ₂ , 2 MPa IP* (N ₂); acetone extraction	38.4 ^b	[110]
<i>Dunaliella tertiolecta</i>	28.4 ^b	8.6%(TS)*; 360 °C, 50min, Na ₂ CO ₃ ; CHCl ₃ extraction	30 ^c	8.6% (TS)*; 360 °C, 50 min, Na ₂ CO ₃ ; CHCl ₃ extraction	30.7 ^b	[52]
<i>Dunaliella tertiolecta</i>	11.4 ^a	5.5% (TS)*360 °C, 60 min, K ₂ CO ₃ ; CHCl ₃ extraction	32 ^c	5.5% (TS)*360 °C, 60 min, K ₂ CO ₃ ; CHCl ₃ extraction	30.7 ^b	[49]
<i>Enteromorpha prolifera</i> *	11.4 ^a	12% (TS)*; 300 °C, 30 min, Na ₂ CO ₃ , 2 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	23	12% (TS)*; 300 °C, 30 min, Na ₂ CO ₃ , 2 MPa IP* (N ₂); CH ₂ Cl ₂ extraction	29.9 ^a	[50]
<i>Chlorella pyrenoidosa</i>	21.3 ^a	20% (TS)*; 270 °C, 30 min, 0.7 MPa IP* (N ₂); toluene extraction	39 ^c	20% (TS)*; 300 °C, 30 min, 0.7 MPa IP* (N ₂); toluene extraction	38.5 ^b	[39]
<i>Scenedesmus</i>	22.7 ^a	20% (TS)*; 300 °C, 30 min, 10–12 MPa (N ₂); CH ₂ Cl ₂ extraction	45	20% (TS)*; 300 °C, 30 min, 10–12 MPa (N ₂); CH ₂ Cl ₂ extraction	35.5 ^b	[43]
Defatted <i>Scenedesmus</i>	21.3 ^a		36		35.3 ^b	
<i>Spirulina</i>	17.7 ^a		31		35.8 ^b	
<i>Chlorella vulgaris</i>	24.6 ^a	9% (TS)*; 350 °C, 60 min, Na ₂ CO ₃ ; CH ₂ Cl ₂ extraction	20	9% (TS)*; 300 °C, 60 min, Na ₂ CO ₃ ; CH ₂ Cl ₂ extraction	37.8 ^a	[75]
<i>Spirulina</i>	23.4 ^a		27	9% (TS)*; 300 °C, 60 min, KOH; CH ₂ Cl ₂ extraction	39.9 ^a	
<i>Chlorella vulgaris</i>	22.2 ^a	9% (TS)*; 350 °C, 60 min, Pt/Al 20 MPa (N ₂); CH ₂ Cl ₂ extraction	39	9% (TS)*; 350 °C, 60 min, Pt/Al, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	37.9 ^a	[46]
<i>Nannochloropsis oculata</i>	26.5 ^a	9% (TS)*; 350 °C, 60 min, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	34		38.2 ^a	
<i>Chlorella vulgaris</i>	22.2 ^a	9% (TS)*; 350 °C, 60min, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	35	9% (TS)*; 350 °C, 60 min, Na ₂ CO ₃ , 20 MPa (N ₂); CH ₂ Cl ₂ extraction	37.1 ^a	[47]
<i>Nannochloropsis oculata</i>	26.5 ^a		35	9% (TS)*; 350 °C, 60 min, HCOOH, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	39 ^a	
<i>Spirulina</i>	23.9 ^a		34	9% (TS)*; 350 °C, 60 min, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	36.8 ^a	
<i>Porphyridium cruentum</i>	22.3 ^a	9% (TS)*; 350 °C, 60 min, Na ₂ CO ₃ , 20MPa (N ₂); CH ₂ Cl ₂ extraction	29	9% (TS)*; 350 °C, 60 min, HCOOH, 20 MPa (N ₂); CH ₂ Cl ₂ extraction	36.3 ^a	
<i>Laminaria saccharina</i>	11.2 ^a	9% (TS)*; 350 °C, 15 min; CH ₂ Cl ₂ extraction	25 ^c	12% (TS)*; 350 °C, 60 min; CH ₂ Cl ₂ extraction	36.5 ^a	[45]
<i>Nannochloropsis sp.</i>	18.8 ^a	21% (TS)*; 350 °C, 60 min, 3.5 MPa IP* (He); CH ₂ Cl ₂ extraction	43 ^c	21% (TS)*; 350 °C, 60 min, 3.5 MPa IP* (He); CH ₂ Cl ₂ extraction	39 ^a	[32]
	18.5 ^a	22% (TS)*; 350 °C, 60 min, Pd/C, 0.7 MPa IP* (H ₂); CH ₂ Cl ₂ extraction	57 ^c	22% (TS)*; 350 °C, 60 min, Pd/C, 3.5 MPa IP* (H ₂); CH ₂ Cl ₂ extraction	40.1 ^b	[34]
<i>Desmodesmus sp.</i>	22.0 ^a	9% (TS)*; 375 °C, 5 min, 0.1–0.5 MPa IP* (He); CH ₂ Cl ₂ extraction	49	9% (TS)*; 400 °C, 60 min, 0.1–0.5 MPa IP* (He); CH ₂ Cl ₂ extraction	36.9 ^a	[41]
				9% (TS)*; 375 °C, 5 min 0.1–0.5 MPa IP* (He); CH ₂ Cl ₂ extraction	37.3 ^b	[56]
<i>Chlorella sorokiniana</i>	21.7 ^a	10% (TS)*; 300 °C, 60 min; CH ₂ Cl ₂ extraction.	28	10% (TS)*; 300 °C, 60min; CH ₂ Cl ₂ extraction.	43.7 ^a	[40]
<i>Nannochloropsis salina</i>	25.4 ^b	10% (TS)*; 240 °C, 20 min; CH ₂ Cl ₂ extraction.	30	10% (TS)*; 260 °C, 60 min; CH ₂ Cl ₂ extraction.	38.4 ^a	[42]
		20% (TS)*; 350 °C, 30 min; acetone extraction	46	20% (TS)*; 350 °C, 30 min; acetone extraction	38.1	[78]
<i>Spirulina platensis</i>	20.4 ^b	20% (TS)*; 375 °C, 10 min; acetone extraction	38	20% (TS)*; 310 °C, 30 min; acetone extraction	35.2	
<i>Nannochloropsis sp.</i>	22.4 ^b	25% (TS)*; 260 °C, 60 min; acetone extraction	59 ^c	15% (TS)*; 260 °C, 90 min; acetone extraction	35.6 ^b	[81]
<i>Chlorella sp.</i>	32.3 ^b	25% (TS)*; 220 °C, 90 min; acetone extraction	87 ^c	15% (TS)*; 300 °C, 60 min; acetone extraction	37.4 ^b	
Wastewater culture algae	12.9 ^b	25% (TS)*; 300 °C, 60 min, 0.7 MPa IP* (N ₂); toluene extraction	49 ^c	25% (TS)*; 320 °C, 60 min, 0.7 MPa IP* (N ₂); toluene extraction	33.3 ^a	[80]

* HHV: higher heating value (MJ/kg); daf: dry ash-free basis; TS: total solids of algae; and IP: initial pressure.

^a Calculated according to HHV (MJ/kg)=0.3383 × C+1.442 × (H–O/8) (Dulong's formula).

^b Measured by oxygen bomb calorimeter.

^c Adjusted oil yield (daf%)=oil yield (dry basis %) × 100/(100–ash(%)).

As shown in Fig. 2 the inorganic compounds are distributed in different stages of E2E. Some metal elements in aqueous products can be used for algae growth [37]. However, the inorganic metals in high concentrations may have a negative effect on algae HTL [71]. A detailed discussion of this negative effect is presented in Section 3.2.1.

HTL of algae (Fig. 2) is not only to generate multiphase products, but also to separate and reuse nutrients, water and CO₂ to support the next cycle of algae growth. Therefore, HTL has the potential to resolve the bottlenecks of current algae biofuel including the consumption of water, fertilizer, and energy input. For instance, it has been demonstrated that 0.4 t of biocrude oil is produced from 1 t of dry algae biomass via HTL; about 70–75% of nitrogen and 35–80% of phosphorus along with amounts of other inorganic nutrients remained in the post-HTL aqueous phase [19,69]. In addition, about 75% of the total HTL gas product is CO₂. The post-HTL water and CO₂ can be reused to feed algae, supporting the recycling of nutrients and capturing of CO₂ [37].

Recently, there has been some exploratory study toward algae HTL. Garcia Alba et al. [41,65] suggested that HTL might be most suitable as post-treatment technology in an algae biorefinery. A systematic study indicated that the integration of algae HTL and algae growth could lead to the increase of biomass up to 10 times [69]. The previous study demonstrated the important role of HTL in sustainable energy/chemicals production, as well as environment protection. Besides biocrude oil production, a number of research groups have paid attention to the potential of HTL for valuable chemicals production. For instance, concomitant extraction of biocrude oil and polysaccharides (e.g., α -glucan) from *Chlorella sorokiniana* was carried out by a unique two-step sequential HTL technology [40,42,72]. Another

example was the oriented production of organic acids (e.g., acetic acid, formic acid, etc.) using acid- or base-catalyzed HTL [73].

As a result, E2E paradigm centered on HTL simultaneously maximizes biocrude oil (or chemicals) yield, improves water quality, and captures CO₂, which brings two challenging issues “Energy generation” and “Environmental Protection” together to complement rather than to compete with each other [70]. Unlike the traditional process through which energy generation (i.e. combustion) could easily bring out environmental problem, the E2E paradigm integrates biocrude oil production through HTL, and post-HTL water treatment and CO₂ capture through algae growth.

However, several bottlenecks have to be resolved before the application of HTL for an algae biorefinery. First, biocrude oil produced via HTL has high contents of O and N elements, and needs further deoxygenation and denitrogenation before its application as the transport fuel. Second, aqueous products generated through HTL contain oxidative and toxic compounds (e.g., phenols, pyridines), which may inhibit algae re-growth while being recycled as nutrients. The detailed discussions of these challenges are presented in Sections 4.2 and 5.2.

3. Research advances of algae HTL

The study of HTL from biomass has been reported since 1970s [20]. However, it is relatively new at converting algal biomass into biocrude oil. The development of HTL of algae can be divided into three periods according to its academic activities (Table 1): pioneering time (1994–1999), silent time (2000–2008), and renaissance time (2009–present).

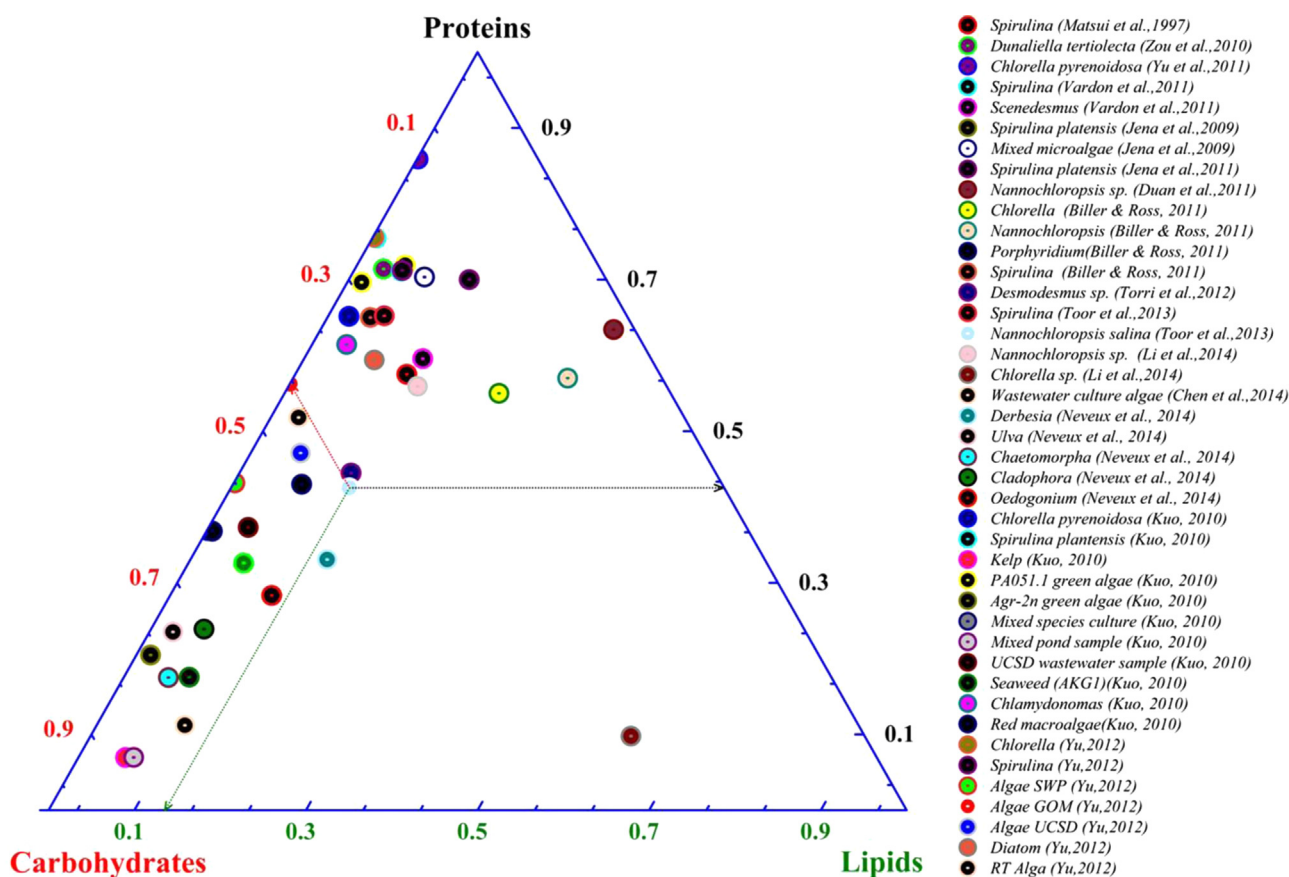


Fig. 3. Characteristics for algae used for HTL. The green, black and red dashed arrows indicate the mass fraction of lipids, proteins and carbohydrates (daf), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Research interest is highly dependent on the cost of conventional crude oil [74]. Table 1 summarizes the research advances on HTL of algae for biocrude oil production, including algae species and higher heating value (HHV), operational conditions, and oil yield and HHV. Dote et al. [23] studied HTL of microalgae in 1994, seemingly the first report of its type. They found the biocrude oil yield (64%) from *Botryococcus branunii* via HTL was higher than the original lipids content (50%) in the feedstock. Therefore unlike biodiesel production by extracting lipid from algae, the biocrude oil production via HTL mainly depends on the amount of algal biomass rather than its lipid content.

As summarized in Table 1, the most important operational conditions for HTL of algae include holding temperature, retention time of holding temperature, TS of feedstocks and catalysts. In the last five years, there has been growing interest in the study of algae HTL, indicating a promising alternative to the current algae–biodiesel route. Key operational parameters, such as TS (5–50%), holding temperature (200–380 °C), and retention time (5–120 min), have been investigated for algae HTL. To date, the maximum yields of biocrude oil are about 50–80%, partly employed catalysts [25,27,34,46,75]. So far, the reported top value of biocrude oil yield was 78.3% based on dry ash-free basis (daf) of feedstock using *Spirulina* as the feedstock and under the HTL condition at 350 °C, 60 min, and 5 MPa initial pressure [25].

The optimal conditions for oil yield were usually different from those of oil HHV. The oil yield was defined as the percentage of the dry basis (db) of biocrude oil versus daf. Note that the research on biocrude oil production via HTL is in its infancy stage, and the concept has not been well established. Specifically, the biocrude oil yield highly depends on the separation procedure of HTL products [36,39,42,44] and the solvent used [76] for extracting biocrude oil. In this review, biocrude oil yields (daf%) have been adopted.

3.1. Algae species and characteristics used for HTL

Algae, including microalgae [19,23–28,31–34,36,38–53,56,75–81] and macroalgae [45,50,54,71,79,82–84], have been used for HTL. Microalgae used for HTL include *Spirulina* [25,31,35,36,38,47,75], *Dunaliella* [24,26,48,49,51–53], *Chlorella* [19,39,40,42,46,75,81], *Nannochloropsis* [33,34,47,75,81], *Scenedesmus* [38,43,46], *Desmodesmus* [41,56], natural mixed microalgae [31,80], etc., which were originally used as food or special chemicals.

Fig. 3 describes algae characteristics for HTL using a ternary diagram. In Fig. 3, the green, black and red dashed arrows indicate the contents of lipids, proteins and carbohydrates, respectively, which are main organic components of algae. As shown in Fig. 3, most algae used for HTL have low lipids content, usually < 20% (daf). Algae having low lipids content, means high proteins or carbohydrates relatively.

Lipids are non-polar aliphatic compounds, which are principally referred to triacylglycerides. Lipids are water insoluble under ambient conditions. Carbohydrates include polysaccharides, starch, cellulose and hemicellulose. Lignin together with cellulose and hemicellulose are called lignocelluloses. Lignocelluloses are major components of some plants and macroalgae, which are also the main components of cell wall [85,86]. Proteins are major components of algae, which consist of at least one peptide chain. Nitrogen is the key element for proteins [87]. Proteins also contain sulfur, and there are some sulfur-containing amino acids, such as methionine and cysteine [88]. The sulfur contents in algae usually are low compared to other major elements such as carbon, hydrogen and nitrogen. However, algae may have higher sulfur and nitrogen contents than other types of biomass. For instance, Bi and He [89] reported that the nitrogen and sulfur contents in microalgae were 1.6–6.8% and 0.4–1.0% (db), respectively. In comparison, Ross et al. [90] reported oat straw contained

1.06% nitrogen and less than 0.2% sulfur (db). Some nitrogen and sulfur contained in proteins may be released to the biocrude oil via HTL, resulting in the release of odor and negatively affecting combustion and other properties of biocrude oil. Brown et al. [32] found that during HTL of *Nannochloropsis* sp., the sulfur contents in biocrude oil increased from 0.4% to 1.0% (db), corresponding to a S/C (mol/mol) ratio of 0.002–0.005 with the increase of holding temperature from 200 °C to 450 °C. Thus it is important to understand the degradation of proteins for HTL of algae [56,75].

Compared with cornstarch and other lignocellulosic biomass, many microalgae with low carbohydrates can be easily converted into biocrude oil with higher oil HHV due to their low content of oxygen [86]. The distribution of the main components in algae is highly dependent on growth conditions and might be different even for the same species [3,91].

Besides the industrial single microalgae, natural mixed algae are also considered as a HTL feedstock. Jena and Das [31] carried out algae liquefaction using both a single (*Spirulina*) and natural mixed algae from open ponds fed with wastewater. Algal blooms have been considered as serious pollution of lakes and sea coasts due to water eutrophication, and their biomass can be used as feedstocks for biofuel [92–94]. Algae could be also co-liquefied with coal through HTL. Ikenaga et al. [27] examined the co-liquefaction of microalgae such as *Chlorella*, *Spirulina*, and *Littorale Yallournor*, with Illinois no. 6 coal in 1-methylnaphthalene under hydrogen at 300–400 °C.

One key difference of biocrude oil via HTL conversion and biodiesel from algae extraction is the dependency on lipids content of algae [6,18,29]. Fig. 4 shows the relations between algal biomass and lipid content. As illustrated in Fig. 4, algae with high lipids content were commonly associated with slow growth rates and low biomass productivities [91,95–97]. This was because high lipids content was usually caused by nutrient limitation [98], which negatively impacted algae growth and biomass accumulation [91].

For biodiesel production, lipids content was the main criterion for screening suitable algae species [6] and demanded growing of pure algae species which could tremendously increase the operational cost [2]. Natural algae are almost all fast-growing with high proteins and low lipids. One of the advantages of HTL is that all organic components of algal biomass, not limited to lipids, can be converted into biocrude oil [39,43]. As for the reaction conditions, water serves as both solvent and reactant [13]. Therefore, HTL is

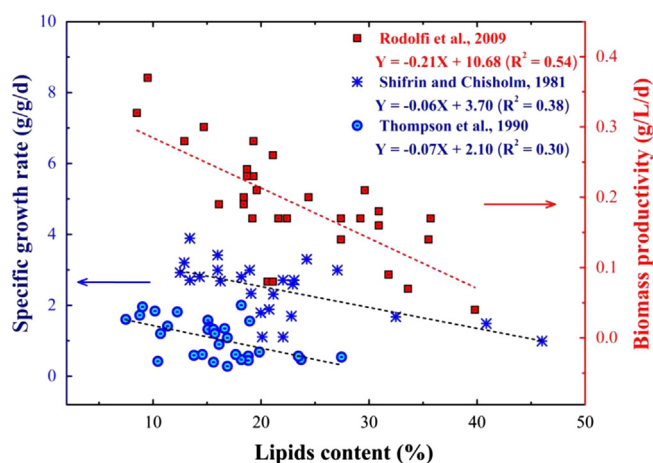


Fig. 4. Relationships between specific growth rate, biomass productivity and lipid content. Figure was drawn derived from Refs. [91,95–97]. Specific growth rate (μ) is defined as the increase in cell mass per day (g/g/d). It was calculated as $\mu = [\ln(m_2) - \ln(m_1)] / (t_2 - t_1)$, where “ \ln ” is the natural logarithm function, and “ m_t ” is the cell biomass at the different time ($t_2 > t_1$); Biomass productivity is defined as the increase in cell density per day (g/L/d).

suitable for converting different wet biomass, including low-lipids algae, into biocrude oil. However, high-lipid algae may require simpler processes for post-HTL oil upgrading and refining than other algae strains.

3.2. Effects of operational conditions on HTL

HTL using hot compressed water as the solvent has the advantages of being abundant, non-toxic and non-flammable, inexpensive and naturally stored in biomass [9]. Most previous studies on HTL of algae were conducted under milder subcritical

conditions [11]. Water under subcritical condition is a unique and sustainable reaction medium, which has its specific characteristics of environmental benign nature and tunable physical properties [13]. HTL conducted in a single fluid phase has the advantages of higher concentrations of reactants, no limits from mass transfer and easy separation of products due to the polar differences of water and products [13]. The enthalpy of water phase change at high pressure is largely reduced during HTL, leading to a reduced latent loss and enhanced energy efficiency. The effects of different organic solvents, such as methanol, ethanol and 1,4-dioxane on HTL, were systematically studied [77], suggesting that methanol

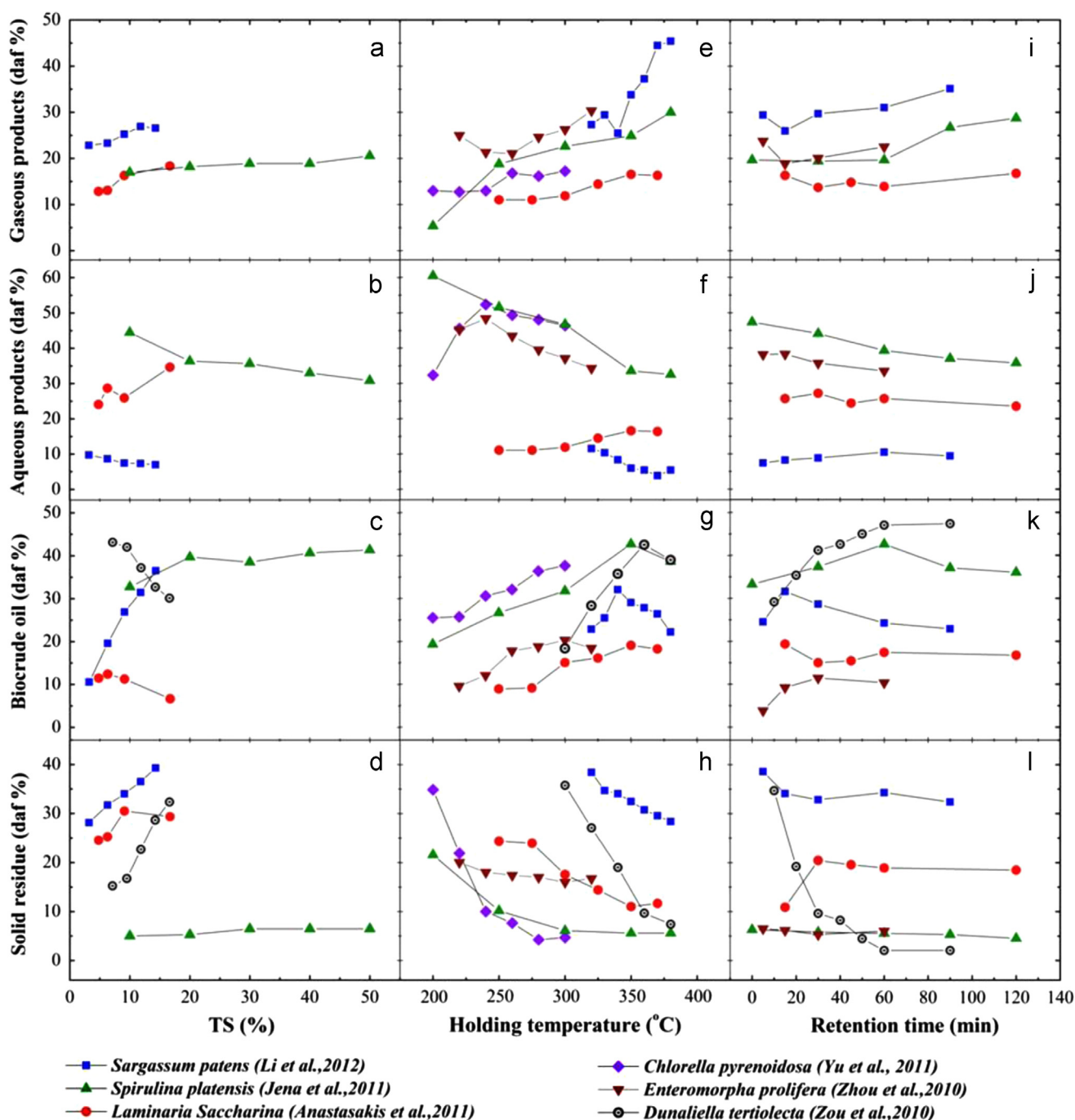


Fig. 5. Effects of major operational parameters on the distribution of products via algae HTL. The products yields (%) were calculated based on dry ash-free basis (daf). Operation conditions were as follows: Li et al. [54]: 340 °C, 15 min (Fig. 5a–d); 30% (TS), 15 min (Fig. 5e–h); 20% (TS), 340 °C (Fig. 5i–l); Jena et al. [35]: 350 °C, 60 min (Fig. 5a–d); 20% (TS), 60 min (Fig. 5e–h); 20% (TS), 350 °C (Fig. 5i–l); Anastasakis et al. [45]: 350 °C, 60 min (Fig. 5a–d); 12% (TS), 15 min (Fig. 5e–h); 12% (TS), 350 °C (Fig. 5i–l); Yu et al. [39]: 20% (TS), 30 min (Fig. 5e–h); Zhou et al. [50]: 12% (TS), 30 min (Fig. 5e–h); 12% (TS), 300 °C (Fig. 5i–l); Zou et al. [51]: 360 °C, 30 min (Fig. 5c–d); 8.6% (TS), 30 min (Fig. 5g–h); 8.6% (TS), 360 °C (Fig. 5k–l).

and ethanol enhanced the conversion rate and oil yield compared with 1,4-dioxane. The biocrude oil generated in methanol contained higher carbon and hydrogen concentrations and lower oxygen content, resulting in a increased HHV [76]. However, a key challenge for HTL with organic solvent was its high cost [8,9]. Operational parameters for HTL of algae in recent studies include feedstock selection [47,75], TS of algae [36], holding temperature [23,24,28,32,36,41], retention time of holding temperature [24,28,36,41], and catalyst selection [23,24,28,34,47,75]. Fig. 5 presents the effects of typical operational parameters on the distribution of products via HTL of algae [36,39,45,50,51,54]. The HTL working volume is usually 50–2000 mL (Table 1) under the process conditions of 200–400 °C and 10–120 min retention time. As illustrated in Fig. 5, though the analysis of whole products in different phases was carried out by few research groups [36,39,45,50,54], the importance of products except biocrude oil has not yet been well recognized from the perspective of biorefinery.

Algae have less lignocellulosic content than other biomass, such as cornstalk. In this section, we focus on discussing the effects of operational conditions including TS of algae, holding temperature and retention time on the performance of HTL of algae and products distribution.

3.2.1. TS of algae

The selection of TS used in HTL depends on many factors, such as algae species, the scale of the reactor and economics [35,55]. Most studies for HTL of algae were investigated with TS of 10–30% although TS < 10% was suggested using marine algae as feedstocks, such as *Dunaliella tertiolecta* [48,51,52] and *Laminaria Saccharina* [45] (Fig. 5a–d). However, there is no clear relationship between TS and oil yield. More issues related to mass transfer, thermochemical conversion and energy consumption may occur if the TS are too high, whereas the volume efficiency and productivity of the HTL reactor will be reduced if the TS are too low. Anastasakis et al. [45] studied the reasonable concentration of input feedstocks in a batch reactor using brown macroalgae *Laminaria saccharina* as feedstock. The influence of TS, retention time, holding temperature and catalyst (KOH) addition was assessed. A maximum yield of biocrude oil (19%) was obtained at 9% TS, 350 °C and 15 min without using any catalyst [45]. Jena et al. [35] examined HTL of *Spirulina* slurry with TS of 10–50%. It is not straightforward whether the results were applicable for other algae species, although little influence of TS was found in the biocrude yield. Compared with microalgae *Spirulina platensis* (Fig. 5), solid residue was increased with the increase of TS for macroalgae *Sargassum patens*, indicating that microalgae could be more easily converted into biocrude oil than macroalgae.

3.2.2. Organic components and HTL

The HTL of organic components in algae includes three steps [99,100]: (1) hydrolysis of proteins, carbohydrates and lipids; (2) decomposition of amino acids, fatty acids and sugars; and (3) recombination and decomposition of reaction intermediates. Based on the liquefaction of model organic compounds, including protein, starch and glucose, triglyceride and amino acids [39,52], Biller and Ross [47] applied the following equation to estimate the biocrude oil yield:

Biocrude oil yield (%) = [protein content (%) × protein yield (%)] + [carbohydrate content (%) × carbohydrate yield (%)] + [lipid content (%) × lipid yield (%)].

The potential yields for converted algae components into biocrude oil via HTL were reported in the order: lipids > proteins > carbohydrates [47].

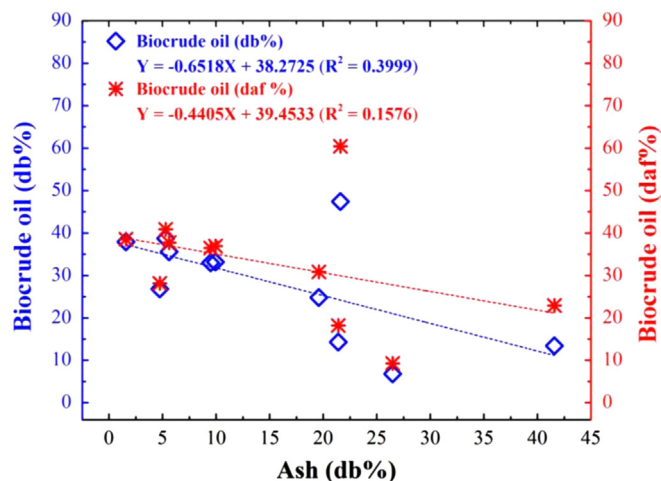


Fig. 6. Effect of algae ash contents on biocrude oil production. Figure was drawn derived from Kuo [83].

3.2.3. Ash and HTL

Fig. 6 illustrates negative effects of algae ash on biocrude oil production in HTL [83]. This is due to two aspects. First, a high ash content means less organic materials converted into biocrude oil and more solid residue left. Second, more ash could cover the surface of organic matter [101] and further hamper mass transfer and thermal chemical reaction of organic matter with subcritical water [71]. Natural mixed algae were usually found containing more ash, less proteins and lipids, resulting in less biocrude oil production [31]. In particular, macroalgae have higher ash than microalgae, resulting in lower yields of biocrude oil [45,54]. Note that there is no quantitative relation between ash content and biocrude oil since biocrude oil yield is affected by many factors and highly dependent on algae species and organic components. For instance, Chen et al. [80] recently reported a biocrude oil yield of 49.9% (daf) from mixed-culture algae with a high ash content of 47.5% (db). Thus the effects of ash content on HTL still need further study.

According to the experimental formula from Channiwala and Parikh [102], HHV can also be negatively affected by the contents of oxygen, nitrogen and ash with the following relationship:

$$\text{HHV} = 0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times \text{ash}.$$

More research is needed for better understanding of the ash effect on HTL.

3.2.4. Holding temperature

As illustrated in Fig. 5e–h, holding temperature has a remarkable influence on the performance of HTL. In general, more oil and gases are converted when holding temperature is increased until 320 °C; meanwhile, solid residue and aqueous products are decreased. Several authors reported the concentration of CO₂ reduced once the temperature rose above the critical point of water, whereas more small hydrocarbon gases (CH₄, C₂H₆, etc.) were produced [32,36,54]. The reported small amounts of CO might indicate that either the removal of oxygen during HTL was mainly achieved by decarboxylation instead of decarbonylation [56], or CO reacted with water and forms CO₂ and H₂ by the water–gas shift reaction [103].

Suitable holding temperature varies depending on algae species (Fig. 5). Many studies used holding temperature which were at 300–350 °C, as illustrated in Fig. 5e–h [36,45,51,52,54]. However, high oil yields were also reported at 250–300 °C using *Enteromorpha prolifera* [50], *Chlorella pyrenoidosa* [39,50] as

feedstocks. Holding temperature was selected depending on the competition of hydrolysis, fragmentation, repolymerization and other reactions [99,100,104]. Depolymerization of algae biomass is a dominant reaction during the initial stage, repolymerization becomes active at later stages that lead to the formation of char [11,44]. A higher heating rate usually leads to higher amounts of biocrude oil yield [22,105].

Yu et al. [19] suggested that carbon recovery and nitrogen recovery of HTL products were also affected by holding temperature. The biocrude oil yield using *Chlorella* as feedstocks tended to increase when holding temperature increased up to 350 °C, and then declined as more gases are formed at higher holding temperature [19]. As holding temperature increased, carbon recovery and nitrogen recovery of biocrude oil decreased but aqueous products increased. After HTL, parts of carbon and nitrogen in the algae feedstock remained in aqueous phase. Yu et al. [19] also indicate that the sum carbon recovery of biocrude oil and aqueous products reached about 91%, while the sum of nitrogen recovery was nearly 100% at 300 °C. The changes of carbon recovery and nitrogen recovery suggest that the gaseous products yield was negligible at lower holding temperature (< 160 °C), then rose at higher holding temperature (240–300 °C) [19]. This study proved that the formation of algal biocrude oil was closely related to deoxygenation and denitrogenation, which will be further discussed in Section 4.2.

3.2.5. Retention time of holding temperature

Retention time is another important operational parameter affecting the product distribution of HTL. Most studies have demonstrated that biocrude oil yield is a function of retention time, and a range of 30–60 min is commonly suggested for HTL (Fig. 5i–l). However, the optimal retention time still highly depends on the critical time point when oil yield has already reached its maximum. For instance, as shown in Fig. 5k–l, Zou et al. [51] reported that biocrude oil was increased while solid residue was decreased with the increase of retention time from 10 min to 60 min at 360 °C. Anastasakis et al. [45] found that

biocrude oil declined while solid residue rose with the increase of retention time from 15 min at 350 °C.

The mechanism of retention time on the degradation of algal components has not been well understood. For instance, cyclic oxygenates were found in the aqueous products [56] and the role of retention time on their production is not clear. Some amino acids in aqueous products, such as alanine and glycine, firstly increased and then decreased with the increase of retention time [106]. This result indicates that the intermediates, such as amino acids, produced from protein via HTL were not stable. One example is the Millard reaction, which takes place between amino acids from protein and reducing sugar from carbohydrates [106,107].

3.2.6. Catalysts

Catalysts are undoubtedly important for chemical reactions, which could affect the reaction rate, the composition of products, and the quality of oil [108]. Table 2 is a summary of catalysts used for HTL of algae. Both homogeneous (alkali, alkali salts, etc.) and heterogeneous catalysts (metallic oxide, etc.) were used for the catalysis of HTL of algae [46,75]. The results of HTL using catalysts were not all positive (Table 2). One study reported higher oil yield and HHV were achieved without catalysts [46] than with catalysts. Ross's group has carried out systematic investigations on catalysts for HTL of microalgae [45–47,75] towards biocrude oil with high oil quality and low molecular weight from low-lipid algae, including *Chlorella vulgaris* and *Spirulina*. Catalysts employed include alkali, potassium hydroxide, sodium carbonate, and organic acids. The yields of biocrude oil were in the descending order of the catalysts used: Na₂CO₃ > CH₃COOH > KOH > HCOOH [75]. Biller et al. [46] reported that the use of heterogeneous catalysts enhanced the deoxygenation of biocrude oil. Co/Mo/Al₂O₃ and Pt/Al₂O₃ seemed to selectively deoxygenate carbohydrates and proteins, whereas Ni/Al₂O₃ preferred deoxygenating lipids, supported by more alkanes formed in the biocrude oil. The use of Ni/Al₂O₃ catalysts also appeared to promote gasification [46]. Carbon deposition [108] was found on the surface of catalysts after HTL, which might reduce

Table 2
Summary of catalysts used for HTL of algae.

Catalyst	Algae species	Algae HHV* (MJ/kg)	Optimal biocrude oil yield (daf%)*	Optimal biocrude oil HHV* (MJ/kg)	Ref.
Na ₂ CO ₃	<i>Botryococcus branunii</i>	34.2 ^a	64	50.2 ^a	[23]
	<i>Dunaliella tertiolecta</i>	19.8 ^a	40	37.8 ^a	[24]
	<i>Microcystis viridis</i>	26.1 ^a	64	31 ^a	[28]
	<i>Dunaliella tertiolecta</i>	28.4 ^b	30 ^c	30.7 ^b	[48]
	<i>Enteromorpha prolifera</i> *	11.4 ^a	29	29.9 ^a	[50]
Fe(CO) ₅ –S	<i>Spirulina</i>	18.8 ^a	61	33.2 ^a	[25]
Na ₂ CO ₃ , NiO, Ca ₃ (PO ₄) ₂	<i>Spirulina platensis</i>	19.6 ^a	55.2 ^c (Na ₂ CO ₃)	38.4 ^b (Ca ₃ (PO ₄) ₂)	[110]
Na ₂ CO ₃ , KOH, CH ₃ COOH, HCOOH	<i>Chlorella vulgaris</i>	24.6 ^a	20 (Na ₂ CO ₃)	37.8 ^a (Na ₂ CO ₃)	[75]
	<i>Spirulina</i>	23.4 ^a	27 (Na ₂ CO ₃)	39.9 ^a (KOH)	
	<i>Chlorella vulgaris</i>	22.2 ^a	34 (Pt/Al)	37.9 ^a (Pt/Al)	
Co/Mo/Al ₂ O ₃ , Ni/Al ₂ O ₃ , Pt/Al ₂ O ₃	<i>Nannochloropsis oculata</i>	26.5 ^a	39	38.2 ^a (Pt/Al)	[46]
	<i>Chlorella vulgaris</i>	22.2 ^a	35	37.1 ^a (Na ₂ CO ₃)	
Na ₂ CO ₃ , HCOOH	<i>Nannochloropsis oculata</i>	26.5 ^a	35	39 (HCOOH)	[47]
	<i>Porphyridium cruentum</i>	22.3 ^a	29 (Na ₂ CO ₃)	36.3 ^a (HCOOH)	
	<i>Spirulina</i>	23.9 ^a	34	36.8	
	<i>Chlorella sorokiniana</i>	18.5 ^a	57 ^c (Pd/C)	40.1 ^b (Pd/C)	
Zeolite, Pd/C, Pt/C, Ru/C, Ni/SiO ₂ –Al ₂ O ₃ , CoMo/γ–Al ₂ O ₃					[34]

The operational conditions used in cited references are referred to Table 1.

* HHV: higher heating value (MJ/kg); daf: dry ash-free basis.

^a Calculated based on HHV = 0.3383 × C + 1.442 × (H – O/8).

^b Measured by oxygen bomb calorimeter.

^c Adjusted oil yield (daf%) = Oil yield (dry weight%) × 100/(100 – ash(%)).

the contact area between feedstocks and noble metal atoms, and further decrease the activity of catalysts.

Homogeneous catalysts employed for HTL are acids (H_2SO_4 , HCl and acetic acid), metal ions (Zn^{2+} , Ni^{2+} , Co^{2+} , and Cr^{3+}), salts and alkalis (CaCO_3 , Ca(OH)_2 , HCOONa , and HCOOK [109]; Na_2CO_3 , NiO , $\text{Ca}_3(\text{PO}_4)_2$ [110]). Alkalis are often used to break up carbon–carbon bond; thus beneficial for the formation of gases [111]. Acids and alkalis enhance the hydrolysis of algal biomass, while metal ions favor the dehydration during HTL [111]. Based on the conversion efficiency and yield of aqueous products, the catalytic activity is in the following order: $\text{K}_2\text{CO}_3 > \text{KOH} > \text{Na}_2\text{CO}_3 > \text{NaOH}$ [112].

So far, the majority of the work has focused on homogeneous catalysis by acid, alkali or metal salts partly because homogeneous catalysts are cheap. Compared with heterogeneous catalysts, the main characteristics of homogeneous catalysts are aqueous products without suffering from coking [108]. However, homogeneous catalysts have the drawbacks of special requirement on HTL reactor material and being difficult to recycle [99,100]. In comparison, heterogeneous catalysts have the advantages of reaction selectivity and post-HTL separation. Recently heterogeneous catalysts have received increasing attention, in particular the development of non-noble metal based catalysts [108]. However, there is a long distance before its application to HTL.

3.2.7. Initial pressure and gas type

The main purposes of applying initial pressure are to maintain water in liquid phase, reduce the enthalpy of phase change of water, enhance the solubility of biomass and improve the energy efficiency [9,113]. A common method is using inert nitrogen to replace the air inside the HTL reactor and keep the reactor in an oxygen-free atmosphere [39]. Reducing gases, such as CO and H_2 , were also investigated in the early study of HTL in order to further reduce the oxygen content of biocrude oil [25]. However, at least one study has shown that the effect of reducing gas was not very significant [114].

A previous study showed that HTL of algae was hardly affected by the initial pressure [39], whereas HTL of cattle manure was negatively impacted by initial pressure [115]. More solid residues were produced at higher initial pressure, which could have resulted from the repolymerization of biocrude oil due to reduced activation energies [99,100,103,104,116].

4. Process mechanism analysis of algae HTL

4.1. HTL reaction mechanism

The mechanism of HTL of algae has not yet been clearly elucidated. Quantitative reaction models based on the governing reaction network are needed for reactor design and process optimization. To closely track all products streams, rather than only pursue biocrude oil on the energy purpose, a systematic analysis was given here based on the literature data. As discussed in Section 2, the operational conditions of HTL such as holding temperature and retention time significantly affect the distribution of products. A simplified scheme [9,11,44,117] for the hydrothermal processes is presented (Fig. 7). The hydrothermal processes can be classified into three types according to different operational conditions (Fig. 7): (1) hydrothermal carbonization (HTC) for the production of solid biochar; (2) HTL for the production of biocrude oil; and (3) hydrothermal gasification (HTG) for the production of syngas. A similar characteristic for three processes is that aqueous products are formed since water is involved for all routes (Fig. 7).

In addition, Fig. 7 shows that the hydrothermal conversion of biomass is established by mimicking the formation of natural fossil

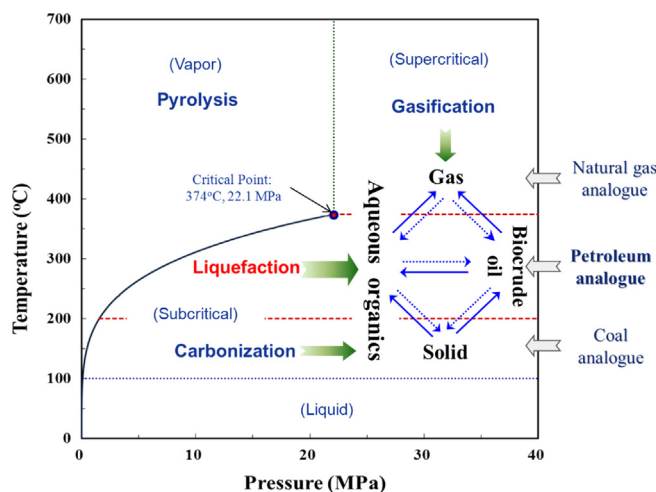


Fig. 7. A simplified scheme for the hydrothermal processes. Figure was drawn derived from [9,11,44,117]. The area between the two red dash lines is the reaction zone for HTL. The relations between four phase products (biocrude oil, solid, aqueous organics, and gases) were made based on the dominant products of the three hydrothermal processes (hydrothermal liquefaction, hydrothermal carbonization and hydrothermal gasification) and HTL kinetic pathways. Aqueous organics exist in all of the three hydrothermal processes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fuels including petroleum, natural gas and coals [118]. According to biogenic hypothesis of oil and gas, all fossil fuels found in nature are formed through hydrothermal conversion of biomass buried beneath the ground for millions of years under the conditions of high temperature and pressure [12,118]. Hydrothermal conversion is a process with physical and chemical changes of biomass in a heated, pressurized and oxygen-free closed reactor, where algal biomass with long-chain organic compounds is firstly broken into short-chain components, such as hydrocarbons [44,119]. As HTL starts, the yields of gases, aqueous products and biocrude oil increase. The pathway from algae to aqueous products represents the release of intracellular proteins and carbohydrates, and their subsequent decomposition during HTL [44]. The pathway to biocrude oil represents the decomposition of the cell wall, hydrolysis of the phosphor lipids and reforming of produced small molecules [44]. Intracellular lipids are also released and hydrolyzed as HTL continues [44]. Part of biocrude oil is converted into gaseous products [77], although it is not clear whether gaseous products originate from biocrude oil. Part of biocrude oil might also be converted to the aqueous products, such as triglycerides and phosphorous [106,107]. An example is that lipids are hydrolyzed and converted into glycerol via hydrolysis of triglyceride [120] and phosphates via hydrolysis of phospholipids [121,122]. Reactions as such could account for the slight increase of yields of aqueous products with the increase of retention time.

As previously described in Section 3.2.2 and Fig. 5, holding temperature is a decisive parameter for controlling the hydrothermal conversion of biomass. For example, a HTG will be enhanced when holding temperature is beyond the suitable range for HTL (Fig. 7) [36]. As illustrated in Fig. 7, different temperature zones resulted in different distributions of products.

4.2. Deoxygenation and denitrogenation of HTL

Algae biomass consists of a mixture of organic and inorganic components. The elements contained in algal biomass are carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, potassium, sodium, etc. [2,3]. Most of the elements in biomass exist as either heteroatoms with the carbon or ions [3,85]. Only carbon and hydrogen can

be used for hydrocarbon liquid fuels. Oxygen and nitrogen are main elements supporting the growth of algae, which, however, are undesirable for crude oil purpose. Oxygen itself has no heating value, and nitrogen will cause environment pollution if combusted [85]. From these view, biocrude oil formation via HTL is accompanied with deoxygenation [86,116] and denitrogenation [56].

Fig. 8 is a two-screen van Krevelen diagram of algae and their biocrude oil [25,31,34,36,38,41,43,46,47,49,51,56,75,78]. As illustrated in Fig. 8(a), most algal biocrude oil has lower H/C than pyrolysis oil, whereas most algal feedstocks and their biocrude oil have lower O/C than pyrolysis oil, indicating the unique features of algae. *Botryococcus branunni* is a specific strain, and the biocrude oil of which has higher H/C than petroleum. However, the O/C and N/C are relatively higher. As shown in Fig. 8, O/C and N/C are significantly reduced during the conversion of algae into biocrude oil through HTL, which demonstrates that HTL is an effective process to harvest carbon and hydrogen and redistribute other elements (oxygen, nitrogen, etc.) into other products (aqueous and gaseous products). However, oxygen and nitrogen contents in the biocrude oil are still high and negatively affect its application as transportation fuel, compared with conventional crude oil [86,116]. In most studies as indicated inside the dotted elliptic in Fig. 8, H/C atomic ratio was reduced from 1.5–2.5 to 1.0–2.0 with the decrease of O/C atomic ratio from 0.3–1.0 to 0–0.3 and N/C atomic ratio from 0.1–0.25 to 0.04–0.1 during HTL [43,45,50].

In comparison, petroleum has an average H/C of 1.84, an O/C of 0.01 and an N/C of below 0.01 according to Hunt [118], as illustrated in Fig. 8. Thus biocrude oil still needs upgrading to reduce O/C and N/C although H/C is similar to petroleum. The changes of O/C had a stronger relationship with changes of H/C than those of N/C.

There were some exceptions as shown outside the dotted elliptic curves in Fig. 8. For instance, N/C was not changed during HTL [43,45,50] especially for natural macroalgae with low N/C [123]; however, N/C could be reduced for HTL of low N/C microalgae by using a sequential HTL [40,42]; distinguished from most studies, H/C was slightly increased with the decrease of O/C and N/C during HTL using *Dunaliella tertiolecta* [24] and *Chlorella pyrenoidosa* [19,39] as feedstocks. These contradictory results reveal the complexity of HTL and the effect of feedstock. In general, HTL led to a stronger promotion on deoxygenation than denitrogenation (Fig. 8). Oxygen could be removed through decarboxylation and dehydration [100]. The decarboxylation is accompanied with the removal of the carbon atom, whereas the latter with the removal of the hydrogen atom [99,100].

Outside the dotted elliptic curves, there were some data with specific levels of O/C, N/C and H/C. For instance, HTL of *Botryococcus branunni* led to the biocrude oil of N/C comparable to petroleum, and a higher H/C [23]. By using a sequential HTL procedure for *Chlorella sorokiniana* [40,42], the O/C and H/C levels of biocrude oil were similar to some kinds of biodiesel and plant oil, and the N/C could reach to the level of petroleum.

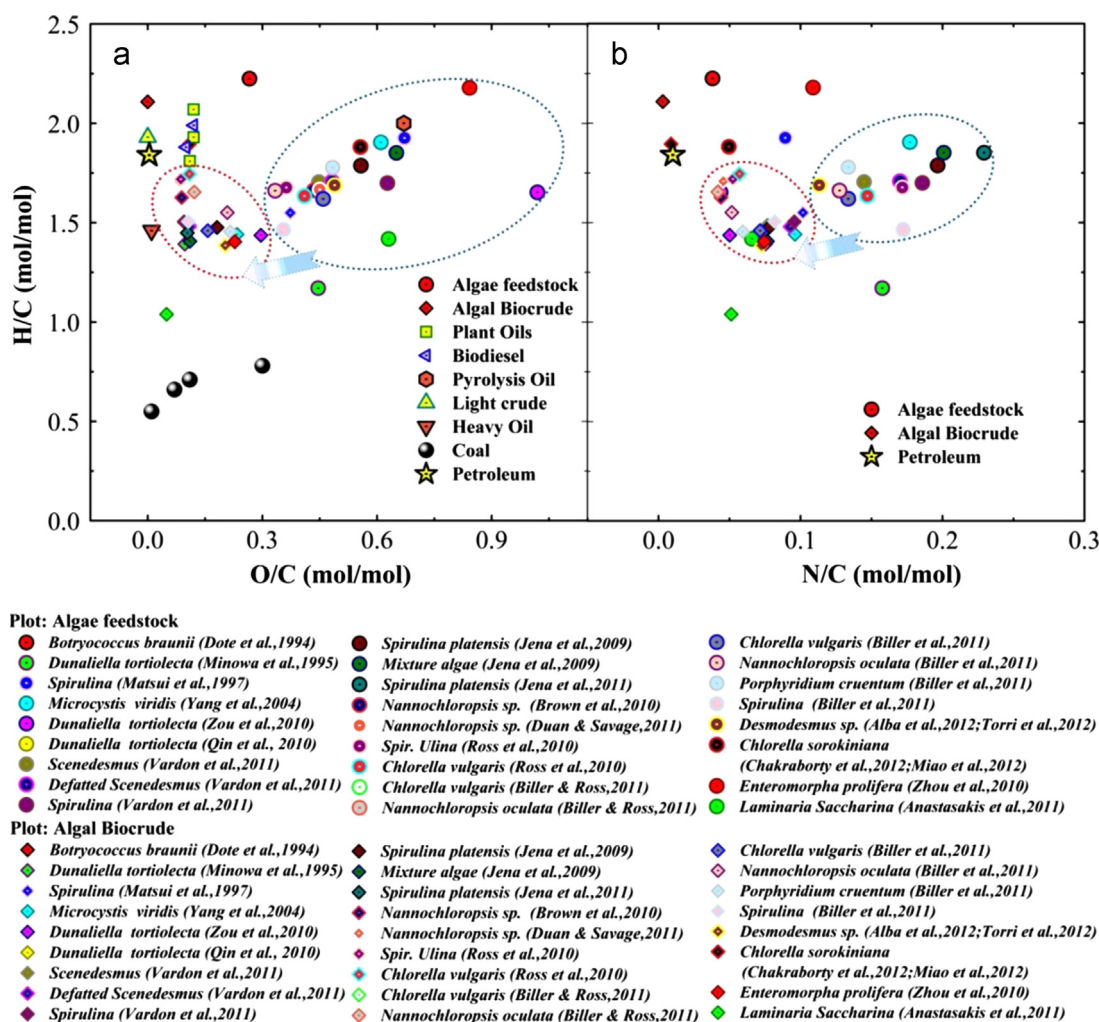


Fig. 8. Van Krevelen diagram of algae and biocrude oil. (a) Deoxygenation during algae HTL. (b) Denitrogenation during algae HTL. The arrows designate the changes of H/C, O/C and N/C from algae feedstock to algal biocrude oil through HTL. The operational conditions used in cited references are referred to Table 1 for biocrude oil yield. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Analysis of biocrude oil shows that oil components varied substantially depending on the feedstocks and operational conditions. However, further research needs to be conducted to elucidate the mechanisms. In order to investigate the mechanisms of deoxygenation and denitrogenation for algae HTL, a number of studies were carried out focused on model compounds that attempted to explore fundamental reaction pathways [103,122,124].

4.2.1. Deoxygenation

The oxygen content of hydrocarbon liquid fuels is less than 1% [118], whereas algal biomass has around 40–60% oxygen [11]. Thus deoxygenation is a main task for converting biomass into hydrocarbon fuels. Fig. 8(a) presents a comparison of algal biocrude oil and other fuels, including biodiesel, pyrolysis oil, plant oil, light crude oil, heavy crude oil and coal [75]. O/C of most algal biocrude oil was similar to that of plant oil and biodiesel, and lower than pyrolysis oil, suggesting HTL results in higher energy density of biofuels than pyrolysis. Oxygen is preferentially removed as H₂O, CO₂ and CO through deoxygenation of algae [103], which itself has no heating value, thus preserving as much heating value of feedstock as possible. Deoxygenation will also result in the increase of H/C, thus leading to a more desirable fuel product [19]. Decarboxylation is a more attractive form of deoxygenation than dehydration due to more oxygen removal [99,100]. Decarboxylation could be controlled using alkali like KOH which was found efficient to enhance decarboxylation [125].

4.2.2. Denitrogenation

Nitrogen content in biocrude oil impacts the properties of biocrude oil, such as smell and combustion [106,107]. Protein is a major component of algal biomass. Fractions of nitrogen in proteins will be decomposed and reformed via HTL, which is called denitrogenation [99,100,106,107]. The reforming of nitrogen via HTL has the advantage of reducing the potential for NO_x emissions during the combustion of biocrude oil [106,107]. Previous work has also suggested that nitrogen in biocrude oil may be difficult to remove through upgrading [126]. The high nitrogen content of the biocrude oil is therefore considered as one of the bottlenecks hindering the development of algae HTL from the perspective of transportation fuel [56].

The hydrolysis of proteins to amino acids prior to HTL may help reduce the nitrogen content of biocrude oil [44]. For instance, 19 amino acids were investigated for biocrude oil production and had oil yields of 2–10% [126]. Nitrogen was released in aqueous products as ammonium and organic nitrogens, whereas only 2–7% of nitrogen was distributed to the biocrude oil. During hydrolysis of algal biomass, amino acids and sugars could also react with each other through the Maillard reaction [106,107,127]. The reaction lead to the formation of nitrogen containing cyclic organic compounds like pyridines and pyrroles, which are common components in biocrude oil. These compounds also act as free-radical scavengers and inhibit free-radical chain reactions that are highly relevant for gas formation [106,107]. In a study using cellulose and ammonia as feedstocks, the increase of N/C of feedstock resulted in the increase of biocrude yield and nitrogen content, and the decrease of solid residue [123], similar to those illustrated in Fig. 8(b) [40,42]. Another study also demonstrated that nitrogen content remarkably affected oil yields and nitrogen contents through HTL by using feedstock of nitrogen-rich albumin and nitrogen-poor sewage sludge [128]. Studies on nitrogen distribution of HTL products showed that a part of nitrogen was released to aqueous products as ammonium ions, whereas the rest was transferred into either biocrude oil as nitrogen heterocycles or the gases as NH₃ and HCN, depending on operational conditions [75]. Homogeneous catalysts, such as Na₂CO₃, could

reduce the nitrogen content of the biocrude oil [123,128]. Compared to carbon distribution as the research focus of HTL, nitrogen distribution receives little attention, but is crucial for sustainable algal biofuels. In particular, nitrogen distributed to gaseous products, such as NH₃ or HCN, has not been investigated for HTL of algae at this time of review.

5. HTL products characteristics and utilizations

The HTL end products, especially the liquid products, need to be separated. Most researchers simply calculated the yield of aqueous products as the difference of feedstock and the total mass collected from biocrude oil, gaseous products, and solid residue [34,36,41,75] due to the limitation of products recovery methods. Products separation procedure is important for HTL of algae because high efficient products recovery is an important insurance for further application of HTL. Definitions used in HTL products, especially the biocrude oil products, need to be clarified based on the separation, solvent, and extraction procedure.

5.1. Biocrude oil

Biocrude oil converted from algae via HTL has an energy content about 70–95% of petroleum based on HHV (Table 1). The physical and chemical properties of biocrude oil strongly depend on feedstocks and HTL operational conditions [38]. The majority of compounds of biocrude oil are dichloromethane or acetone soluble. The heating value of most biocrude oil is in the range of 30–38 MJ/kg [11,38]. When yields are obtained by weighing the solvent extracted material after evaporation of the solvent, the biocrude yield should be treated with caution because it is difficult to clearly separate the solvent and the products with lower boiling point. Biocrude oil is a complex mixture with a large number of compounds and a broad distribution of molecular weight [38]. In general, major compounds identified by Gas Chromatography–Mass Spectrometry (GC–MS) consist of cyclic nitrogenates (e.g., pyrrole, indole, pyrazine, and pyrimidine compounds), cyclic oxygenates (e.g., phenols and phenol derivatives with aliphatic side-chains), and cyclic nitrogen and oxygen compounds (e.g., pyrrolidinedione, piperidinedione, and pyrrolizinedione compounds) [38]. Biocrude oil from algae via HTL needs to be upgraded through catalytic HTL [16,17,33,129], primarily to remove oxygen and nitrogen, and finally produce hydrocarbon fuels. Another alternative for oil utilization is to extract value-added chemicals (e.g., sugars and phenols, and the N-containing amides and nitriles), which may involve nitrogen or oxygen compounds from biocrude oil [16,17,33,129].

5.1.1. Biocrude oil upgrading

Different from crude oil, the biocrude oil has high contents of oxygen and nitrogen, and high molecular weight (or viscosity) [15–17,38]. Biocrude oil therefore needs to be firstly upgraded by hydrodeoxygenation. The addition of hydrogen to the biocrude oil should be performed not to saturate the aromatic rings, but to remove oxygen [74]. Hence, the hydrodeoxygenation process is applied. Biocrude oil via HTL of algae also requires further catalytic process to remove nitrogen and sulfur [86]. After the biocrude oil is catalytically hydro-treated to remove oxygen and nitrogen, oxygen is partly removed as CO₂ or H₂O through deoxygenation and nitrogen is partly converted into ammonium through denitrogenation, which can be fed back for algae growth [58].

Biocrude oil requires milder conditions for upgrading than fast pyrolysis oil, which usually requires 2–3 reactors in series. Typical conditions for hydro-treating are 250–420 °C, 6.9–13.8 MPa [9,58,86]. A single hydrotreater at continuous operation was found

to be able to reduce oxygen content down to 1% and nitrogen content to <0.3% [58]. Catalyst deactivation was not observed during short-term testing [58]. The effluent of hydrotreater is cooled to condense the produced water and hydrocarbon. The organic phase is then separated into four parts according to the differences of their boiling points: C₄ minus, gasoline, diesel, and heavy oil [58]. The heavy oil is assumed to be cracked in a conventional hydrocracker to produce additional products of gasoline and diesel. Detailed analysis of upgraded HTL products and their applications should be further researched.

5.2. Aqueous products

Aqueous products are generated in all three hydrothermal processes (HTL [28,130], HTC [131] and HTG [132]) because water is involved in all the conversions. The utilization of the post-HTL aqueous products plays an essential role on the overall effectiveness [28,130]. The main constituents of post-HTL aqueous include NH₄⁺, PO₄³⁻, and metallic ions, such as K⁺, Na⁺ and Mg²⁺ [28,130–132]. Algae can assimilate nitrogen from a wide variety of sources, and some algae strains have demonstrated their capability to grow in post-HTL wastewater [37,60,61,63,64,69]. For instance, Jena et al. [37] compared the growth of *Chlorella minutissima* in the media containing aqueous products (generated via HTL of *Spirulina*) as sole nutrient source and a standard medium (BG11) for 12 days. The biomass productivity of the former (0.035 g/L/d) was lower than that in BG11 (0.07 g/L/d). The remaining organics in aqueous products, such as O-containing sugars and N-containing amides [130], may be also interesting as carbon sources for heterotrophic algae strains. Aqueous products can be also gasified under supercritical conditions to obtain a hydrogen-rich fuel gas [58], and can be used as reducing gases for biocrude oil upgrading.

HTL is an effective process to destroy biological contaminants in the original biowaste, and at the same time create new toxic chemical substances. The potential toxic compounds which may have inhibitory effects on algal growth contain nitrogenous compounds [130], phenols or phenolics (e.g., catechol and hydroquinone) [133,134]. For instance, Pham et al. [130] identified nitrogenous organic compounds in aqueous products and characterized the mammalian cell cytotoxicity. Their results showed that the descending rank order for cytotoxicity was 3-dimethylamino-phenol > 2,2,6,6-tetramethyl-4-piperidone > 2,6-dimethyl-3-pyridinol > 2-picoline > pyridine > 1-methyl-2-pyrrolidinone > σ -valerolactam > 2-pyrrolidinone > ϵ -caprolactam. The inhibitory mechanism may be attributed to the auto-oxidation of the toxic compounds (e.g., polyphenols) under alkaline conditions in the presence of di- or tri-valent metal ions (such as Mg²⁺) by forming radicals and thus making them toxic [37]. However, Garcia Alba et al. [135] reported that the lack of nutrients was the main reason for growth limits rather than toxicity due to insufficient aqueous products. In addition, toxic chemical substances could be effectively removed through biochemical reactions during algae metabolism [136]. Interestingly, N-containing contaminants involved in post-HTL wastewater may be degraded and converted into NH₄⁺ or NO₃⁻ via algal growth and metabolism [137]. One study indicated that 30% of the toxicity was removed by recycling post-HTL wastewater back into algae cultivation [130].

5.3. Gaseous products

Gaseous products present a yield of around 10–20% of feedstock [32,37,41], primarily CO₂ and other small amount of CH₄, H₂, C₂H₄ and C₂H₆ [32]. Part of nitrogen in feedstock could also be converted into ammonia depending on HTL reaction conditions [75]. Both CO₂ and ammonia gas can be fed back for

autotrophic algae cultivation [5], enhancing multi-cycle reuse of nutrients and carbon.

5.4. Solid residue

Solid residue consists of inorganics and remaining organic matter after HTL of algae [9,11]. Solid residue is normally ash, rich in inorganics. The yield of solid residue highly depends on ash content in the feedstock [31]. With respect to typical cultured algae with low content of ash (<10%), solid residue after HTL was also low (<10%) [36,38]. However, solid residues were increased using high ash algae (>30%), such as algal blooms used for HTL. As discussed in Section 3.2.4, the remaining ash contains inorganics and salts, which might be recycled for algae cultivation [37,60,61,63,64,67,68]. New catalysts might be also extracted from ash [138], which is an interesting research topic yet to be studied.

6. Prospective and challenges

Due to its unique advantages regarding feedstock types and energy efficiency, HTL is expected as a promising technology for algal biorefinery. HTL of algae can provide unprecedented amounts of feedstocks, to resolve major issues of current society, such as energy demand and environment pollution. Prospective and challenges for HTL within the algal biorefinery based on E2E are discussed below.

6.1. Feedstock preparation

As discussed in Section 3.1, HTL could utilize the whole algal biomass for biocrude oil and chemicals. The availability of feedstock resources is a great advantage for HTL of algae, including low-lipid content algae and large-scale algae culture [11,22,139], the natural algae from water blooms [140], and even the algae residue after oil extraction [1,43]. The employment of low-lipid algae for HTL reduces the typical limitations faced by algae for biodiesel, such as energy-intensive drying process before extraction, limited biomass productivity and contamination from other organisms for autotrophic algae growth [35,55]. In terms of feedstock used for the biocrude oil production through HTL, algae may achieve a higher oil yield under milder conditions than lignocellulosic biomass, such as cornstalk from the perspective of biomass structure [86].

There are unique advantages and challenges in algal biomass preparation for HTL [9,11]. First, unlike lignocellulosic biomass, the size of algae is so small that grinding is not needed. Second, the water content of algae can be high, for instance, 80–90% for collected natural algal biomass, which is suitable directly for HTL without energy intensive drying; Third, there is no requirement on whether algae culture species are pure or not since the nature of HTL is to convert biomass, not extract oil from the biomass. These features could simplify the dewatering process, reduce additional energy input and increase the feasibilities for scale-up of HTL of algae. However, there is much work for reducing cost and increasing efficiency of algae harvest [141,142]. So far, algae preparation still requires further systemic research and development.

Although algae resources are tremendously abundant for HTL in the E2E scheme, the delivery of feedstock will be a challenge [58]. Different algae species have various performances of HTL depending on their contents of lipids, proteins, carbohydrates, and ash [3]. In general, microalgae have better performance than macroalgae for HTL [11,45,50], since microalgae contains less ash and lignocelluloses. Most of research is therefore focused on HTL of microalgae. Considering the nature of algal biomass and requirement of oil or chemicals, it is crucial to develop methods

to regulate oxygen and nitrogen through pretreatment in situ, or post-HTL [33,56]. Different strategies might be directed on various applications. For instance, denitrogenation is necessary for transport use of biocrude oil [86], but might not be necessary for petroleum derivative chemicals that prefer nitrogen-containing compounds [116]. Pretreatment technologies for reducing ash content are also needed for high-ash algae, such as macroalgae or algal blooms [50,143] in HTL biocrude production.

6.2. Application of algae HTL

Although it is a promising technology, algae HTL is still in the early stage for biofuel production and environment protection [10,11,144]. HTL has been already tested for various types of biomass, and algae HTL testing in continuous-flow [145,146] and pilot plant [147,148] began in 2013. A deep understanding of its fundamentals and applicability for algal feedstock is still needed.

6.2.1. Analysis of laboratory work

Almost all previous work on HTL of algae was carried out at laboratory level, as summarized in Table 1. This research included algae screening [11,22], the optimization of HTL conditions [36], the analysis of HTL products [43], the study of reaction pathways [44,56], and the upgrading of biocrude oil [16,17,33,129]. Various kinds of algae species were tested. HTL of algae was carried out with parameters of TS, holding temperature, retention time, pressure, and in some cases catalysts and reducing gases. Two issues are worth highlighting: (1) HTL of algae model compounds, such as proteins, lipids and carbohydrates [10,122], could be used for the prediction of product yields and elucidation of the reaction pathways. Detailed characterizations of all the products and intermediates are needed for understanding the HTL; and (2) upgrading treatment for transportation fuel, other value-added chemicals and their applications. Upgrading of biocrude oil has only recently been carried out with few cases, which can be mostly learned from the refinery of fossil fuel [58]. Other challenges include difficulty in separating the solvent and products with lower boiling point during evaporation of the solvent [22].

6.2.2. Prospective for large-scale HTL process

Much work has been performed towards the application of HTL in the past 30 years, although there are no commercial cases for HTL of algae yet. There were several challenges limiting the commercial application of algae HTL [9,58]: (1) lack of a deep understanding of HTL of algal feedstock characteristics; (2) strict requirement of continuous HTL reactors operated with higher temperatures and pressures. This requires the design of specific thermochemical reactors, slurry delivery, and products separation; and (3) much work needed for biocrude oil upgrading and refining. This is quite different from current procedure for crude oil refining particularly due to the high content of nitrogen in the biocrude oil.

Inexpensive and accessible biomass, such as biowaste [149,150], was used in large scale as feedstock of the HTL to produce biocrude oil before application of algae HTL. Pioneering work of the HTL was done in the 1960s–1980s [151]. In 1969, The Pittsburgh Energy Research Center (PERC) developed the HTL process using lignocellulosic wood as feedstock [151]. Considering the problems of feedstock feeding of PERC's, the Lawrence Berkeley Laboratory (LBL) introduced an additional pretreatment of wood before HTL [151]. In the 1980s, the US Environmental Protection Agency (EPA)'s Water Engineering Research Laboratory developed a sludge-to-oil reactor system fed with undigested municipal sewage sludge [152]. Up to 2004, their first large-scale plant was established with a capacity of converting about 250 t/d

of food waste into around 500 barrels of biocrude oil [153]. As for HTL of biomass and upgrading of biocrude oil and its application in transportation, a hydrothermal upgrading (HTU[®]) process was developed in 1982 by the Shell Research Laboratory [154,155] and further commercial efforts have been made since 2001. In Denmark, a Catalytic Liquefaction (CatLiq[®]) technology [149] has been developed with a feedstock capacity of 20 L/h. In 2011, Licella with Virgin Australia and Air New Zealand established a demonstration plant for the production of jet fuels using woody and other biomass as feedstock via the catalytic hydrothermal reactor (Cat-HTR) [150].

These previous efforts for the application of HTL provide important engineering references for mass production of algal biocrude oil. As previously discussed, HTL of algae is based on full utilization of algal components. Biocrude oil and aqueous phases are two important products in an E2E context, but need to be well separated. The aqueous phase and gases are rich in nutrients and CO₂, respectively that can be recycled for algae cultivation. Aqueous products can be also treated by HTG to produce gases rich in H₂, which can be directly used for deoxygenating in biocrude oil upgrading. Solid residue could also be utilized as fertilizer.

6.3. Algae HTL and E2E paradigm

The production of biocrude oil or chemicals and recycling of nutrients could be economically realized via the E2E paradigm in which HTL is a key component. In this paradigm, HTL plant is located nearby algae production. Algae cultivation is fed with post-HTL wastewater and CO₂ [19,66,67,69,70]. Thus, HTL, algae cultivation and nutrients recycling are integrated in a closed cycle, suggesting that the E2E paradigm has the potential to produce renewable energy and chemicals while protecting environment.

Although E2E paradigm is promising, many aspects need to be achieved before applying the E2E scenario to realize the industrial production including catalysts of HTL and oil upgrading, nutrients recycling, algae cultivation and harvesting, and scale-up. For instance, the recycling and reuse of aqueous products may cause the accumulation of nutrients and inhibitory matter, further affecting the re-growth of algae. Zhou et al. [69] recently reported that it was possible to recycle up to 10 times of nutrients via E2E, suggesting that the potential of nutrients recycling may be explored. In addition, algae cultivation and harvesting is a challenge issue [156] although a number of microalgae have been grown in large scale [88], even using wastewater [157] and some harvesting technologies have been developed [3,158]. Another issue is how to make E2E economically viable. HTL in E2E may have some potential features to make this algal biorefinery feasible. However, this will need to be definitively verified.

6.3.1. Resolving the feedstock bottleneck

The E2E paradigm via HTL may reduce the current limitations of algal biomass production due to its unique features. The HTL can be designed taking the characteristics of both original feedstocks and recycled algae into account, and vice versa. Algae cultivation can also cooperate closely with the operational units of products separation and oil upgrading, where nutrients and resources are released or extracted (Fig. 2). The E2E paradigm could help maximize the algal biomass production through nutrient recycling [68]. The amplified biomass is approximately 5–10 times the original mass of bio-waste [66,69]. As an example, there are around 59 billion m³ wastewater and 0.2 billion ton biowaste produced in the US per year [159]. Based on these data, the amplified algal biomass could be as high as 1–2 billion dry tons per year, corresponding to 0.3–1 billion tons of biocrude oil per year via HTL given that the HTL conversion is

30–50 db%. In comparison, the total demand of petroleum in the US was 1.1 billion tons in 2011 [160].

Current algae-to-biodiesel technology is lipid-dependent and difficult to achieve a high algal biomass production. Current algae biodiesel is not ready to supply 5% of the total oil demand of the US partly because of using an unsustainable demand of water, energy and fertilizer [59,161]. In other words, by producing 60 million tons of oil based on its maximum productivity of algae biodiesel, 6–15 million nitrogen and 1–2 million phosphorus are needed.

6.3.2. Flexible HTL

So far, the “only biofuel” option is unlikely to be economically viable for algae biomass [162]. As previously discussed in Section 5.2, other chemicals can be also produced either from HTL process or other E2E stages. It might be also possible to extract value-added chemicals from biocrude oil since it is complex and contains different cyclic nitrogenates and oxygenates besides hydrocarbon [38].

The HTL can be compatible with current algae conversion technologies. Algae residue after extraction of biodiesel [163] nutrients, such as carotenoid or other high-value products, can be further converted into biocrude oil via HTL [43,49], thus constituting an example of biorefinery of whole algae [164]. Algae have the ability to contribute to resolving the issues of energy and the environment through the E2E paradigm [156,165,166]. Regarding the feedstocks for the HTL, algae can be co-converted with other biomass or organics. In some cases, algae biocrude oil might be benefited by mixing with other biomass. For instance, glycerin [6] is a main side product during the production of biodiesel, which might be mixed with algae and served as co-feedstock and hydrogen donor for in situ catalysis of deoxygenation, thus resulting in increased oil production and quality.

6.3.3. Challenges for energy balance and the E2E system

In an E2E scheme of algae, heat demand for the HTL, algae cultivation and harvest, and product separation should be counteracted by part of the energy output stored in biocrude oil, thus achieving energy independence. As previously described, HTL has a characteristic of enhanced energy efficiency due to reduced enthalpy of phase change of water at high pressure and decreased latent loss. Given that the energy recovery ratio is defined as the energy output of the HTL biocrude against the HTL process energy input for HTL reaction, energy recovery ratios were 3:1 at laboratory scale and 11:1 at pilot-scale when heat exchangers were included [70]. At this time, HTL of algae is a huge systematic engineering undertaking and many successful experiences can be learned from modern petroleum refinery plants and wastewater treatment plants. Unlike other independent processes or just the refinery, the HTL has the challenge of how to integrate separated processes, including upstream algae cultivation and harvest, downstream HTL and product upgrading, and resources recycling.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (21106080), the Chinese Universities Scientific Fund (2012RC030, 15053209) and the National High-Tech R&D Program of China (2012AA051803).

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